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FINAL REPORT

ONR Grant No. N00014-85-K-0641

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Precursors and Thin Polyimide Films with Silicon
and Silicon Oxide Surfaces"**

Performing Organization:

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October 1988



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FINAL REPORT

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"Proposal to Study the Interaction of Polyimide Precursors and Thin Polyimide Films with Silicon and Silicon Oxide Surfaces"

The work performed within the research contract N00014-85-K-0641 produced results, which for the first time allowed us to derive a model for the detailed molecular mechanism of adhesion between a polymer and a metal surface. The spectroscopic characterization of polyimide/metal interface was made possible by a vapor deposition technique used to produce polyimide films sufficiently thin to access the interface by photoelectron spectroscopy and Infrared Reflection Absorption Spectroscopy. The polyimide films were prepared by codeposition of oxidianiline (ODA) and 1,2,4,5 Benzenetetracarboxylic Anhydride (PMDA) onto a surface held at 300 K to form polyamic acid. The polyamic acid was then converted to polyimide by a thermal imidization process at $T > 150^{\circ}\text{C}$. The interaction of the pure constituents ODA and PMDA, and of polyamic acid and polyimide with clean Ag, Au, Cu and $\text{YBa}_2\text{Cu}_3\text{O}_7$ surfaces was studied by X-ray Photoelectron Spectroscopy, Infrared Reflection Absorption Spectroscopy (Ag, Cu, Au), Thermal Desorption Spectroscopy (Ag), NEXAFS (Ag(110)), Scanning Tunneling Microscopy (Au) and Raman Spectroscopy (Ag, Cu). The major results have been published, or are prepared for publication, and are summarized below: *thin films, etc.*

1. Adsorption of PMDA and ODA is dissociative on all surfaces studied. On Ag and Cu surfaces, specific surface species were characterized in terms of their bonding interaction to the substrate. It was shown that the bonding of the PMDA fragment on Ag and Cu surfaces is also present in the polymer films and is one mode of bonding polyamic acid and polyimide to the metal /1-8/.
 2. Solventless polyamic acid undergoes intramolecular and intermolecular rearrangements which lead to the formation of carboxylate ions as found in XPS and IRAAS measurements /8,9/.
 3. Solventless polyamic acid can be imidized to polyimide in one atmosphere of pure oxygen. This allows us to produce polyimide films on 1,2,3 superconductors without affecting the superconduction critical temperature /9/.
 4. The structural changes in a polyimide film as a function of distance from the metal surfaces was determined by IRAAS using polarized light. The IRAAS structural results are consistent with the topography of ultra thin polyimide films as observed by STM /7,12/.
 5. Oxidianiline undergoes a wetting/nucleation phase transition on silver surfaces /12/. Such a behaviour has been observed for metals on metals, but is the first example where such a transition has been observed for organic films on metals.
- 1-9*

Journal Articles

1. M. Grunze and R. N. Lamb, "Preparation and Adhesion of Ultrathin Polyimide Films on Polycrystalline Silver", Chem. Phys. Lett., 133 (1987) 283.
2. M. Grunze and R. N. Lamb, "Characterization of Ultra-Thin Polyimide Films (d=11 Å) Formed by Vapor Deposition of 4,4' Oxydianiline and 1,2,4,5 Benzenetetracarboxylic Anhydride," J. Vac. Sci. Technol., A5 (1987) 1685.
3. R. N. Lamb, J. Baxter, M. Grunze, C. W. Kong and W. N. Unertl, "An XPS Study of the Composition of Thin Polyimide Films Formed by Vapor Deposition," Langmuir, 4, (1988) 249.
4. R. N. Lamb and M. Grunze, "Adhesion of Vapor Phase Deposited Ultra-Thin Polyimide Films on Polycrystalline Silver", Surf. Sci., 204 (1988) 183.
5. M. Grunze, J. P. Baxter, C. W. Kong, R. N. Lamb, W. N. Unertl and C. R. Brundle, "Vapor Phase Deposition and Growth of Polyimide Films on Copper", Proceedings of the American Vacuum Society Topical Conference on Deposition and Growth: Limits for Microelectronics, Anaheim, CA, November 1987.
6. R. G. Mack, H. Patterson, M. R. Cook and C. M. Carlin, "A Raman Spectroscopic Study of Vapor Deposited Poly[N,N'-bis(phenoxyphenyl) pyromellitimide] Films", J. Polymer Sci., in press.
7. M. Grunze, W. N. Unertl, S. Gnanarajan and J. French, "Chemistry of Adhesion at the Polyimide Metal Interface", in Proceedings of the Materials Research Society Symposium on Electronic Packaging Materials Science, Vol. 108, Boston, MA, December 1987, p. 189.
8. "Photoelectron Spectroscopy of Thin Polyimide Films on Au(111) Surfaces" (in German), Diplomathesis, T. Strunskus, Universität Heidelberg (1988) (work performed at the University of Maine).
9. "Preparation of Ultra-Thin Polyimide Films on Ceramic Surfaces", presented at the ACS National Meeting in Los Angeles, CA, September 1988, and prepared for publication.
10. "Laser Raman Spectroscopic Studies of Vapor Deposited 4,4' Oxydianiline Films and Vapor Deposited 4,4' Oxydianiline/Pyromellitic Dianhydride Polyimide Films on Polycrystalline Copper and Silver Substrates", Masters Thesis, Roderick G. Mack, University of Maine, 1988.
11. "Vapor Pressure Measurement of Polyimide Constituents and Chemical Cleaning of Metal Substrates", Ph.D. Thesis, Ossama Elshazly, University of Maine, December 1987.
12. "Infrared Reflection Absorption Studies on Polyimide Constituents and Polyimide Films on Silver and Copper Substrates", S. Gnanarajan, Ph.D. Thesis, University of Maine, December 1988.

ONR Technical Reports

1. "Preparation and Adhesion of Ultra Thin Polyimide Films on Polycrystalline Silver"
2. "Characterization of Ultra Thin Polyimide Films (d-11Å) Formed by Vapour Deposition of 4,4-Oxidianiline and 1,2,3,5-Benzenetetracarboxylic Anhydride"
3. "An XPS Study of the Composition of Thin Polyimide Films Formed by Vapor Deposition"
4. "Vapor Phase Deposition and Growth of Polyimide Films on Copper"
5. "Chemical Cleaning of Metal Surfaces in Vacuum Systems by Exposure to Reactive Gases"
6. "Adhesion of Vapour Phase Deposited Ultra-Thin Polyimide Films on Polycrystalline Silver"
7. "Chemistry of Adhesion at the Polyimide-Metal Interface"
8. "A Raman Spectroscopic Study of Vapor Deposited Poly[N,N'-bis(phenoxyphenyl)pyromellitimide] Films"

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